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Molecular First Hyperpolarizabilities of a New Class of Asymmetric Squaraine Dyes

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Abstract

The molecular first hyperpolarizabilities (β) of a series of asymmetric squaraine dyes were measured by electric-field-induced second harmonic generation; the dyes have negative β -values whose magnitudes are comparable to 4-N, N-dimethylamino-4'-nitrostilbene (DANS).

Keywords: Hyperpolarizability, cyanine, nonlinear optics, EFISH, squaraine, squarylium

We have recently proposed and examined the hypothesis that bond length alternation (BLA) (i. e., the difference between average length of carbon-carbon double and single bonds in a polymethine chain) is a useful parameter to consider when establishing structure-property relationships for nonlinear optical (NLO) molecules.¹⁻⁵ Electric field dependent calculations on $(\text{CH}_3)_2\text{N}-(\text{CH}=\text{CH})_4\text{-CHO}$ show that with increasing applied electric field the geometry of the molecule changes from the neutral polyene structure ($\text{BLA} \approx -0.12 \text{ \AA}$) on the left in Figure 1 to the polar cyanine structure ($\text{BLA} = 0 \text{ \AA}$) and to a highly polar zwitterionic polyene structure ($\text{BLA} = -0.05 \text{ \AA}$). At the same time the molecular first hyperpolarizability (β) initially increases, reaches a peak at roughly $\text{BLA} \approx -0.04 \text{ \AA}$ (closer to the cyanine limit than to the polyene limit), decreases and ultimately becomes negative when BLA is positive. Most donor-acceptor substituted π -conjugated molecules, such as stilbenes and polyenes have positive β that increase as the strength of donors and acceptors increase.^{6,7} Moreover, these chromophores usually have BLA greater than -0.10 \AA and therefore are far from having maximized β .⁸ Rather than starting near the polyene limit and decreasing the magnitude of BLA by searching for stronger donors or acceptors, to optimize β , we have considered introducing asymmetry into highly polarizable cyanine-like structures as an alternative strategy. In this manner, we seek to optimize β (in either a positive or negative peak) sense starting from the cyanine limit where $\text{BLA} = 0$. Squaraine dyes are analogous to cyanine dyes in that they both have two degenerate resonance forms (Figure 2) and both exhibit sharp and intense absorption band in visible or near IR region.⁹ However, unlike ionic cyanines, squaraines are neutral molecules that are suitable for electric-field-induced second harmonic generation (EFISH) measurement.*

We are therefore developing synthetic strategies that leads to asymmetric, soluble squaraines with significant β .[†] Previously, It was demonstrated that symmetric squaraines have large molecular second hyperpolarizabilities (γ) by Dirk *et al.*¹¹

Here we report the optical nonlinearities of a new series of asymmetric squaraine compounds (Figure 3). The dyes were prepared by the condensation between appropriate donors, heterocyclic rings with activated methyl group, and 1-aryl-2-hydroxycyclobutene-3,4-diones (**1**), in a procedure analogous to that developed by Law *et al.*¹² Since asymmetric squaraines tend to decompose during chromatography on silica or alumina, the success of the syntheses hinge upon being able to impart the correct volatility, such that the products crystallize directly from the crude reaction mixtures. However, the volatility of asymmetric squaraines must, at the same time, be high enough for EFISH studies. Depending on the donors, isopentyloxy and methoxy groups of **1** appear to satisfy these criteria. Analytically pure products were obtained in 30-80% yield.^{\$} In polar organic solvents, the asymmetric squaraine dyes 2-7 are in general more stable than [4-(dimethylamino)phenyl](4'-methoxyphenyl)squaraine (**8**) and its derivatives prepared by Law *et al.*¹² For instance, pyridine solution (-O. 1 mM) of **8** decolorized completely in one hour, and the similar solution of **3** or **5** showed little deterioration examined by absorption spectra for days.

EFISH data of β (measured in chloroform with 1.907 μm fundamental radiation¹³) and their zero frequency form β_0 (corrected for dispersive enhancement using the two state model¹⁴) for the asymmetric squaraines 2-7 are shown in Table 1, together with the data of optical absorption maximum (λ_{max}), extinction coefficient (ϵ) and the dipole moment (μ). The β_0 -values of 2-7 range from -24 to -63 $\times 10^{-30} \text{ esu}$

that are comparable to that of prototypical stilbene compound 4-N,N-dimethylamino-4'-nitrostilbene (DANS) ($\beta_0 = 55 \times 10^{-30} \text{ esu}$) but are opposite in sign. The magnitude of the β -values of 2-7 follow roughly the order of conventional donor strength, i.e., lepidinium > quinaldinium; benzothiazolium > benzoselenazolium, benzoxazolium, and indolium.¹⁵ Comparison of β -values between asymmetric squaraines with donors whose structure differ significantly (e.g., lepidinium and benzothiazolium derivatives), is difficult without the knowledge of the μ orientation with respect to the β tensor since EFISH only measures the projection of the β tensor along the dipole direction.

Chromophores with negative β -values are uncommon. However, two examples are merocyanine and dicyanoquinodial compounds.¹⁶ The negative β -values are consistent with the negative solvatochromic behavior of these dyes (e.g., λ_{max} for 3 appear at 562 nm in ethanol, 616 nm in chloroform, and 664 nm in toluene). The negative β -values of asymmetric squaraine dyes suggest that the dyes either have a larger ground- than excited-state dipole or the direction of the dipole moment actually changes sign in the excited-state. Thus, one intriguing question is whether the intramolecular charge-transfer (CT) of asymmetric squaraines involves a shift of charge from one end of the molecules to the other end or only from the one end to the central squaraine ring (C_4O_2). This is not understood at this stage and we are synthesizing model compounds to probe the question.

In summary, by introducing structural asymmetry, we have prepared a new class of asymmetric squaraine dyes that are asymmetric cyanine analogs for NLO second-order applications. Their β -values are substantial and negative in sign. A study of the

dipole moment and the intramolecular CT involved in the optical nonlinearity of asymmetric squaraine is in progress.

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FOOTNOTES

The definition of BLA that we have used for polymethine dye does not directly apply to squaraine dyes, as they have no polymethine chain. The idea of desymmetrizing squaraine may nonetheless be analogous to desymmetrizing cyanine dyes.

† A different type of the asymmetric squaraine, donor 1,2-disubstituted cyclobutene-3,4-dione, has been examined for their powder SHG by Pu and Fu.⁹

‡ Compounds 2-7 gave ¹H NMR, UV-visible, FAB-MASS, fully consistent with the proposed structure. Analytically pure samples were obtained by recrystallization from pyridine and hexanes. Satisfactory elemental analysis were obtained for all compounds except 4. Compound 4 tends to decompose in pyridine. The sample of 4 showed low ratio in carbon: Found(Calculated), C, 70.92(72.61), H, 5.06(4.93), N, 3.95(4.03).

FIGURE CAPTION

Figure 1. A plot of β *versus* bond length alternation (BLA) for

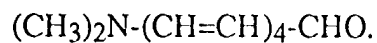


Figure 2. Canonical resonance structures of a cyanine (**A**), squaraines (**B**, **C**, and **D**), and asymmetric squaraines (**E**). X can be O, S, Se, or C(CH₃)₂.

Figure 3. Synthesis of asymmetric squaraines 2-7. Symbol * indicates the active site of donors that react to 1. Here R equals to isopentyl for quinaldinium (2), benzothiazolium (5), and benzoselenazolium (6); methyl for lepidinium (3), benzoxazolium (4), and indolium (7). TsO⁻ denotes *p*-toluenesulfonate.

Figure 1

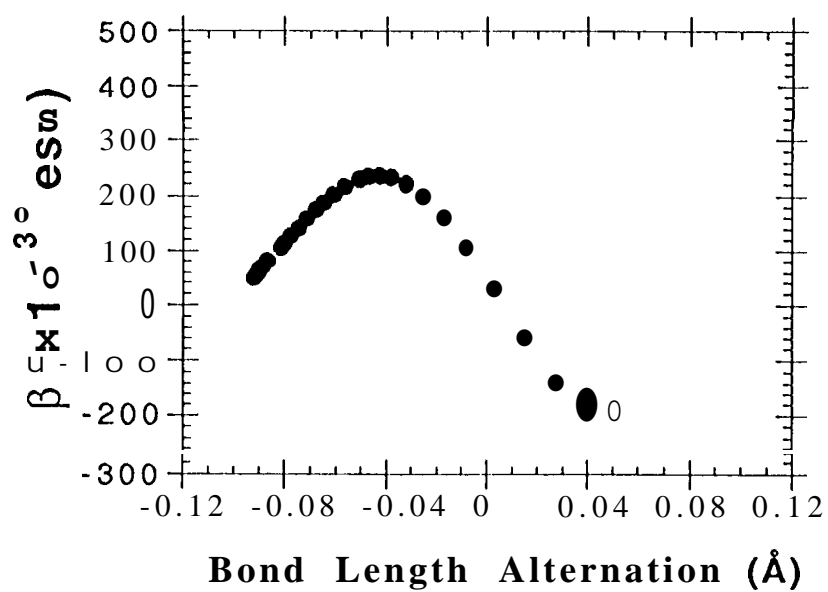


Figure 2

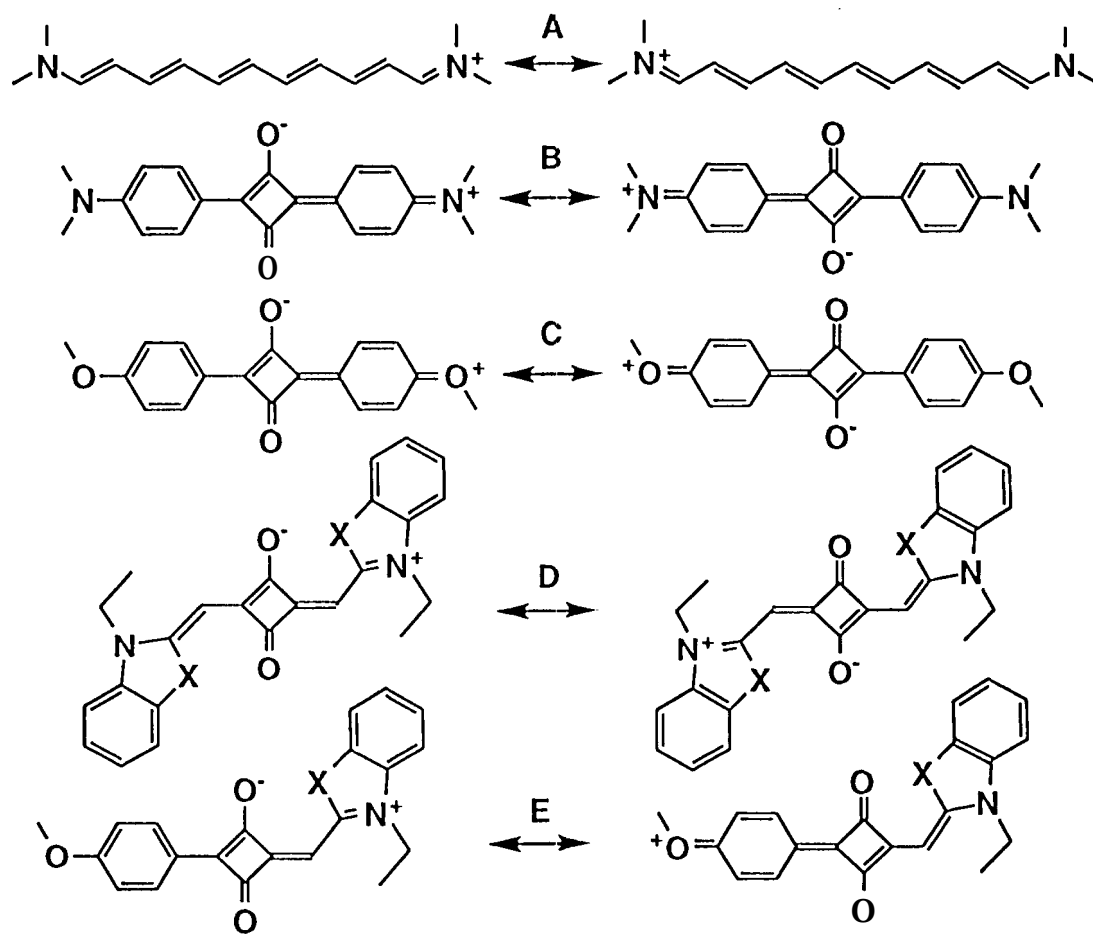
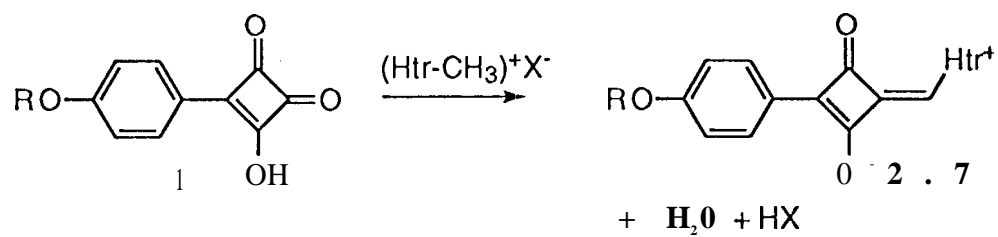
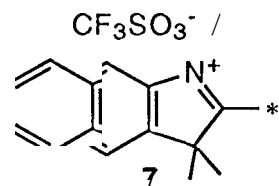
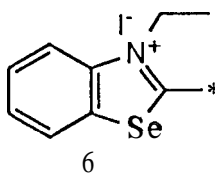
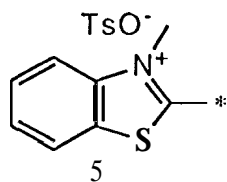
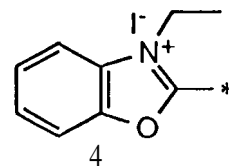
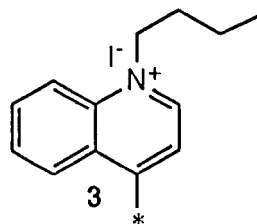
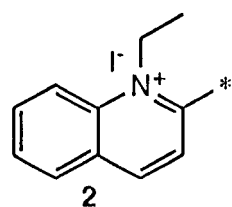


Figure 3



$(\text{Htr-CH}_3)^+\text{X}^- =$



TABLE

Table 1. Optical data of asymmetric squaraines 2-7 measured in chloroform with 1.907 μm as fundamental radiation.

#	λ_{max} (nm)	ϵ ($10^4 \text{M}^{-1} \text{cm}^{-1}$)	μ (10^{-18}esu)	β (10^{-30}esu)	β_0 (10^{-30}esu)
2	572	6.0	7.5	-94	-55
3	616	14	8.5	-120	-63
4	518	9.6	7.5	-42	-27
5	554	10	7.7	-95	-58
6	562	10	6.6	-41	-24
7	556	11	7.5	-69	-42

Supplementary Materials

ELEMENTAL ANALYSIS OF UNSYMMETRICAL SQUARAIN DYES

	Formula	% Found (Calculated)			
		C	H	N	S
2	C ₂₂ H ₂₇ NO ₃	78.34(78.42)	6.61(6.58)	3.42(3.39)	
3	C ₂₅ H ₂₃ NO ₃	77.34(77.90)	5.98(6.01)	3.85(3.63)	
4	C ₂₁ H ₁₇ NO ₄	70.92(72.61)	5.06(4.93)	3.95(4.03)	
5	C ₂₄ H ₂₃ NO ₃ S	71.20(71.08)	5.73(5.72)	3.51(3.46)	7.83(7.91)
6	C ₂₅ H ₂₅ NO ₃ Se	64.44(64.37)	5.41(5.40)	3.01(3.00)	
7	C ₂₃ H ₂₁ NO ₃	76.76(76.86)	5.92(5.89)	3.94(3.90)	

FAB-MASS AND ¹H NMR OF UNSYMMETRICAL SQUARINE DYES

	M m/e (F.W.)	¹ H NMR δ, ppm from TMS*
2	414 (413.49)	9.79(d, J = 9.0 Hz, 1H), 8.68(d, J = 9.0 Hz, 1H), 8.45(d, J = 9.0 Hz, 1H), 8.22(d, J = 7.5 Hz, 1H), 8.11(d, J = 8.7 Hz, 2H), 8.07(t, J = 7.5, 1H), 7.82(t, J = 7.5 Hz, 1H), 7.07(d, J = 8.7 Hz, 2H), 6.51 (s, 1H), 5.03(q, J = 6.5 Hz, 2H), 4.1 l(t, J = 6.9 Hz, 2H), 1.82(m, 1H), 1.68(m, 2H), 0.97(d, J = 6.6 Hz, 6H).
3	386 (386.44)	9.66(d, J = 6.9 Hz, 1H), 9.07(d, J = 6.9 Hz, 1H), 8.80(d, J = 8.4 Hz, 1H), 8.47(d, J = 8.7 Hz, 1H), 8.16(t, J = 7.5 Hz, 1H), 8.10(d, J = 8.7 Hz, 2H), 7.94(t, J = 7.5 Hz, 1H), 7.03(d, J = 8.7 Hz, 2H), 6.96(s, 1H), 4.93(t, J = 7.5 Hz, 2H), 3.86(s, 3H), 2.04(m, 2H), 1.50(m, 2H), 0.98(t, J = 7.2 Hz, 3H).
4	348 (347.35)	8.16(d, J = 9.0 Hz, 2H), 8.05-8.08 (m, 1H), 7.99-8.03 (m, 1H), 7.66-7.70(m, 2H), 7.08(d, J = 9.0 Hz, 2H), 6.32(s, 1H), 4.74(q, J = 7.2 Hz, 2H), 3.88(s, 3H), 1.58(t, J = 7.2 Hz, 3H).
5	406 (405.49)	8.33(d, J = 7.8 Hz, 1H), 8.13(d, J = 7.8 Hz, 1H), 8.09(d, J = 9.0 Hz, 2H), 7.78(t, J = 7.7 Hz, 1H), 7.67(t, J = 7.5 Hz, 1H), 7.06(d, J = 9.0 Hz, 2H), 6.58(s, 1H), 4.30(s, 3H), 4.11 (t, J = 6.6 Hz, 2H), 1.82(m, 1H), 1.67(m, 2H), 0.96(d, J = 6.6 Hz, 6H).
6	468 (466.44)	8.39(d, J = 7.8 Hz, 1H), 8.11(d, J = 7.5 Hz, 1H), 8.08(d, J = 8.7 Hz, 2H), 7.73(t, J = 7.8 Hz, 1H), 7.58(t, J = 7.5 Hz, 1H), 7.06(d, J = 8.7 Hz, 2H), 6.68(s, 1H), 4.85(q, J = 7.1 Hz, 2H), 4.11(t, J = 6.6 Hz, 2H), 1.82(m, 1H), 1.67(m, 2H), 1.53(t, J = 7.1 Hz, 3H), 0.96(d, J = 6.6 Hz, 6H).
7	360 (359.41)	8.21 (d, J = 8.9 Hz, 2H), 7.79(d, J = 6.0 Hz, 1H), 7.81(d, J = 7.5 Hz, 1H), 7.58(t, J = 7.5 Hz, 1H), 7.51(t, J = 7.4 Hz, 1H), 7.11(d, J = 8.9 Hz, 2H), 6.34(s, 1H), 4.06(s, 3H), 3.90(s, 3H), 1.85(s, 6H).

* in d₇-DMF at room temperature recorded by 300 MHz QE-300.